AQUATIC EFFECTS TECHNOLOGY EVALUATION (AETE) PROGRAM

Technical Evaluation on
Sample Collection, Handling,
Analysis and Interpretation for
Trace Level Contamination in Water

AETE Project 3.1.1

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AQUATIC EFFECTS TECHNOLOGY EVALUATION PROGRAM

Notice to Readers

Technical Evaluation on Sample Collection, Handling, Analysis and Interpretation for Trace Level Contamination in Water

The Aquatic Effects Technology Evaluation (AETE) Program was established to review appropriate technologies for assessing the impacts of mine effluents on the aquatic environment. AETE is a cooperative program between the Canadian mining industry, several federal government departments and a number of provincial governments; it is coordinated by the Canada Centre for Mineral and Energy Technology (CANMET). The program was designed to be of direct benefit to the industry, and to government. Through technical and field evaluations, it identified cost-effective technologies to meet environmental monitoring requirements. The program included three main areas: acute and sublethal toxicity testing, biological monitoring in receiving waters, and water and sediment monitoring.

The technical evaluations were conducted to document certain tools selected by AETE members, and to provide the rationale for doing a field evaluation of the tools or provide specific guidance on field application of a method. In some cases, the technical evaluations included a go/no go recommendation that AETE takes into consideration before a field evaluation of a given method is conducted.

The technical evaluations were published although they do not necessarily reflect the views of the participants in the AETE Program. The technical evaluations should be considered as working documents rather than comprehensive literature reviews. The purpose of the technical evaluations focused on specific monitoring tools. AETE committee members would like to stress that no one single tool can provide all the information required for a full understanding of environmental effects in the aquatic environment.

For more information on the monitoring techniques, the results from their field application and the final recommendations from the program, please consult the AETE Synthesis Report to be published in the spring of 1999.

Any comments concerning the content of this report should be directed to:

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PROGRAMME D'ÉVALUATION DES TECHNIQUES DE MESURE D'IMPACTS EN MILIEU AQUATIQUE

Avis aux lecteurs

Évaluation technique de la surveillance de la qualité de l'eau : plan d'échantillonnage et analyse

Le Programme d'évaluation des techniques de mesure d'impacts en milieu aquatique (ÉTIMA) visait à évaluer les différentes méthodes de surveillance des effets des effluents miniers sur les écosystèmes aquatiques. Il est le fruit d'une collaboration entre l'industrie minière du Canada, plusieurs ministères fédéraux et un certain nombre de ministères provinciaux. Sa coordination relève du Centre canadien de la technologie des minéraux et de l'énergie (CANMET). Le programme était conçu pour bénéficier directement aux entreprises minières ainsi qu'aux gouvernements. Par des évaluations techniques et des études de terrain, il a permis d'évaluer et de déterminer, dans une perspective coût-efficacité, les techniques qui permettent de respecter les exigences en matière de surveillance de l'environnement. Le programme comportait les trois grands volets suivants : évaluation de la toxicité aiguë et sublétale, surveillance des effets biologiques des effluents miniers en eaux réceptrices, et surveillance de la qualité de l'eau et des sédiments.

Les évaluations techniques ont été menées dans le but de documenter certains outils de surveillance sélectionnés par les membres d'ÉTIMA et de fournir une justification pour l'évaluation sur le terrain de ces outils ou de fournir des lignes directrices quant à leur application sur le terrain. Dans certains cas, les évaluations techniques pourraient inclure des recommandations relatives à la pertinence d'effectuer une évaluation de terrain que les membres d'ÉTIMA prennent en considération.

Les évaluations techniques sont publiées bien qu'elles ne reflètent pas nécessairement toujours l'opinion des membres d'ÉTIMA. Les évaluations techniques devraient être considérées comme des documents de travail plutôt que des revues de littérature complètes. Les évaluations techniques visent à documenter des outils particuliers de surveillance. Toutefois, les membres d'ÉTIMA tiennent à souligner que tout outil devrait être utilisé conjointement avec d'autres pour permettre d'obtenir l'information requise pour la compréhension intégrale des impacts environnementaux en milieu aquatique.

Pour des renseignements sur l'ensemble des outils de surveillance, les résultats de leur application sur le terrain et les recommandations finales du programme, veuillez consulter le Rapport de synthèse ÉTIMA qui sera publié en février 1999.

Les personnes intéressées à faire des commentaires concernant le contenu de ce rapport sont invitées à communiquer avec M^{me} Geneviève Béchard à l'adresse suivante :

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Executive Summary

Recently, improvements in analytical chemistry technology have given scientists the ability to measure lower and lower concentrations of metals and other contaminants in water. Similarly, as the understanding of the environmental effects of contaminants has increased, the acceptable concentrations in water of many of these contaminants have decreased. When monitoring water quality, it is preferable to be able to reliably measure concentrations of contaminants which are one tenth of the acceptable concentrations of those contaminants.

The validity of reporting data with very low concentrations of contaminants depends on collecting representative samples and ensuring sample integrity, by taking all necessary steps to ensure that, once collected, samples do not deteriorate and are not contaminated. Prior to analysis the integrity of water samples must be maintained during collection, transportation and storage, through the implementation of appropriate quality assurance practices. Possible contamination may be detected and measured through quality control samples.

Great care must be taken during sample collection to prevent contamination, and once collected they must be preserved to ensure that they do not deteriorate prior to analysis. Chemical preservation, storage temperatures and holding time all play a role in sample preservation. During sample collection, preservation, handling, transportation and storage, samples are at risk of contamination. The major sources of water sample contamination include: sample bottles and caps; preservatives; filters; sampling, filtering and laboratory equipment; poor sampling, handling and storage practices; and airborne contaminants (e.g., dust, fumes). Contamination can be minimized by ensuring that all persons involved, including those in the field and in the laboratory are properly trained, and by ensuring that instructions for collecting, transporting and storing samples are well thought out and clearly documented.

Water sample contamination can be monitored with the use of blanks, such as trip blanks, field blanks, equipment blanks, and filtration blanks.

Once samples reach the laboratory, a key consideration in the interpretation of analytical results for samples with very low concentrations of contaminants is the detection limit or limiting low concentrations below which a particular analyte cannot be detected. There are two distinct detection limits that may be reported - the Method Detection Limit (MDL) and the Reliable Detection Limit (RDL). The Method Detection Limit is the measured response at which there is a stated probability (usually 95 or 99%) that the analyte is present. The Reliable Detection Limit is the lowest analyte concentration required to be present in the sample to ensure detection; i.e., the analytical response that will exceed the MDL with stated probability (usually 95 or 99%). The detection limit in most common usage and that best approximates an industry-standard is the MDL (99%), but the RDL represents the point at which measured values become believable. Another limit, the Limit of Quantitation, or LOQ, provides a further assured level of confidence that data which exceed it are statistically significant.

An understanding of the meaning and significance of the different detection limits can aid in the interpretation of low level data, such as very low concentrations of metal in water. For example:

- if: result < MDL then: analyte not detected
- if: MDL ≤ result < RDL then: analyte is present but result is not statistically significant
- if: RDL ≤ result < LOQ then: result is borderline statistically significant at the RDL
- if: result ≥ LOQ then: result is statistically significant

A comparison of water quality guidelines with the detection limits which are commercially available in Canada shows that, for most parameters of interest in a metal mining context, it is possible to measure contaminant concentrations as low as 1/10 of the water quality guideline for those contaminants. When monitoring water quality, it is preferable to be able to reliably measure concentrations of contaminants which are 1/10 of the acceptable concentrations of those contaminants. However, for several contaminants, technology is not currently commercially available to be able to reliably measure concentrations at such low levels. These contaminants include: arsenic, cadmium, mercury, selenium, silver and cyanide. The technology is available at some laboratories in Canada to measure all but cadmium and mercury at 1/10 of the lowest guideline.

SOMMAIRE

Grâce aux améliorations récentes apportées aux techniques de chimie analytique, les scientifiques sont aujourd'hui capables de mesurer des concentrations de plus en plus faibles de métaux et d'autres contaminants dans l'eau. Dans le même ordre d'idées, une meilleure compréhension des incidences des contaminants sur l'environnement a également entraîné une réduction des concentrations de bon nombre de ces contaminants, jusque-là considérées comme acceptables. Dans tout projet de surveillance de la qualité de l'eau, le fait de pouvoir mesurer de façon fiable des concentrations de contaminants équivalentes au dixième de leurs seuils limites respectifs est considéré comme un objectif fort souhaitable.

La validité des données faisant état de très faibles concentrations de contaminants dépend du prélèvement d'échantillons représentatifs et de l'intégrité des échantillons, laquelle n'est assurée que si toutes les précautions nécessaires sont pour prévenir l'altération et la contamination des échantillons après leur prélèvement. Avant de procéder à l'analyse, toutes les mesures d'assurance de la qualité doivent être mises en place pour assurer l'intégrité des échantillons d'eau durant leur prélèvement, leur transport et leur entreposage. On peut constater et mesurer le niveau de contamination possible par un contrôle de la qualité des échantillons.

Durant le prélèvement, il est extrêmement important de prendre toutes les précautions voulues pour prévenir la contamination des échantillons d'eau qui, une fois prélevés, doivent être conservés afin de prévenir leur altération avant l'analyse. L'utilisation d'agents de conservation chimiques et le respect des températures et des durées d'entreposage recommandées jouent un rôle déterminant dans la conservation des échantillons. Les échantillons d'eau peuvent être contaminés en tout temps durant leur prélèvement, leur conservation, leur manipulation, leur expédition et leur entreposage. Les principales sources de contamination incluent les éléments suivants : bouteilles et bouchons/capsules; agents de conservation; filtres; équipement; pratiques d'échantillonnage, de manipulation et d'entreposage fautives ainsi que les contaminants aéroportés (p. ex., poussière, fumée). Il est possible de réduire les risques de contamination en veillant à ce que toutes les personnes qui participent au prélèvement, à la manipulation et à l'entreposage des échantillons, en laboratoire ou sur le terrain, aient reçu la formation et les instructions requises.

Aux fins de la surveillance de la contamination des échantillons d'eau, on peut utiliser des échantillons témoins ou à blanc, comme par exemple des blancs d'expédition, blancs de terrain, blancs d'équipement, et blancs de filtration.

Une fois que les échantillons sont parvenus au laboratoire, un point essentiel à considérer lors de l'interprétation des résultats des analyses des échantillons présentant de très faibles concentrations de contaminants est la limite de détection ou la concentration en-deçà de laquelle il devient impossible de détecter la présence d'un contaminant donné. Il existe deux grands types de seuils de détection - la limite de détection de la méthode (LDM) et la limite de détection fiable (LDF). La LDM est la réponse mesurée à laquelle la présence d'un contaminant donné est considérée comme certaine à seuil de probabilité prédéterminé (habituellement 95 ou 99 %). La LDF correspond à la plus faible concentration d'un contaminant choisi à laquelle sa détection dans l'échantillon devient possible (c.-à-d., résultat d'analyse supérieur à la LDM pour un seuil de probabilité prédéterminé (habituellement

95 ou 99 %). La limite de détection la plus couramment utilisée et celle qui s'approche le plus d'une norme de l'industrie est la LDM (99 %). Pour sa part, la LDF correspond au point à partir duquel les valeurs mesurées deviennent crédibles. Une autre limite, appelé limite de dosage, fournit un autre seuil de confiance dans la mesure où toutes les données qui lui sont supérieures peuvent être considérées comme statistiquement significatives

Une bonne compréhension de la signification des différentes limites de détection peut faciliter l'interprétation des résultats attestant de faibles concentrations (p. ex. très faibles concentrations de métaux dans l'eau). Voici quelques exemples :

- Résultat < LDM : contaminant non détecté.
- LDM ≤ résultat < LDF : contaminant détecté, mais résultat non statistiquement significatif.
- LDF ≤ résultat < limite de dosage - résultat considéré comme près d'être statistiquement significatif à la LDF.
- Résultat ≥ limite de dosage : résultat considéré comme statistiquement significatif.

Une comparaison des critères de qualité de l'eau avec les limites de détection disponibles sur le marché au Canada révèle qu'il est possible, pour la majorité des paramètres qui présentent un intérêt particulier dans le contexte de l'exploitation des métaux, de mesurer des concentrations de contaminants équivalant au dixième des critères de qualité de l'eau établis pour ces mêmes contaminants. Pour la surveillance de la qualité de l'eau, il est préférable de pouvoir mesurer de façon fiable des concentrations de contaminants correspondant au dixième des concentrations acceptables de ces mêmes contaminants. Toutefois, pour plusieurs contaminants, soit l'arsenic, le cadmium, le mercure et le cyanure, les méthodes disponibles actuellement ne permettent pas de mesurer de façon fiable des concentrations aussi faibles. La technologie permettant de mesurer tous les contaminants, sauf le cadmium et le mercure, au dixième des concentrations acceptables les plus faibles pour ces contaminants, est disponible dans certains laboratoires canadiens.

TABLE OF CONTENTS

1 Introduction 1

2 Sampling Collection, Preservation and Handling 2
2.1 Introduction 2
2.2 Water Sample Collection 3
2.2.1 Options for Water Sample Collection 3
2.2.2 Techniques for Reduction of Contamination During Sample Collection 4
2.2.3 *In Situ* Monitoring 6
2.3 Water Sample Preservation 7
2.3.1 Methods of Preservation 7
2.3.2 Monitoring Water Sample Preservation 9
2.4 Water Sample Contamination 10
2.4.1 Minimizing Sample Contamination 10
2.4.2 Monitoring Sample Contamination 13

3 Analytical Detection Limits 16
3.1 Introduction 16
3.2 Types of Detection Limits 17
3.2.1 Method Detection Limit and Reliable Detection Limit 17
3.3.2 Limit of Quantification 18
3.3.3 Consensus Detection Limit 19
3.4 Interpreting Low Level Data 20
3.5 Influence of the Sample Matrix on the Detection Limit 21
3.6 Reporting and Quality Control 22

4 Water Quality Guidelines and Achievable Detection Limits 23
4.1 Overview of Water Quality Guidelines 23
4.2 Achievable Detection Limits 23
4.3 Comparison of Detection Limits and Water Quality Guidelines 27

5 Considerations for the Selection of a Laboratory 31

6 References 33

List of Tables

Table 1: Detection limits achievable for in situ monitoring methods, and water quality guidelines for the same parameters 6
Table 2: Recommended container types, preservation and storage methods, and holding time for various analytes 7
Table 3: Comparison of the Method Detection Limit (MDL), Reliable Detection Limit (RDL), and Limit of Quantitation (LOQ) 19
Table 4: Guidelines for interpreting low level data 20
Table 5: Relationships between sample matrix and effects on detection limits 21
Table 6: Comparison of selected parameter groupings, sample preparation and matrix differences 22
Table 7: Summary of water quality guidelines for selected parameters 24
Table 8: Summary of achievable detection limits 25
Table 9: Comparison of water quality guidelines with analytical methods that have method detection limits which are equal to or less than the guideline value 28
Table 10: Summary of parameters for which a method detection limit (MDL) at least ten times lower than the water quality guideline (WQC) is not currently available 29
Table 11: Comparison of measurement uncertainty at different MDL:Result ratios 29
Table 12: The impact of replicate samples on measurement uncertainty 30

List of Appendices

Appendix 1: Detection Limit Calculation 35

Appendix 2: Considerations in Interpretation of Low Level Data 39

Appendix 3: Summary of Laboratory Responses to Survey of Detection Limits 41

1 Introduction

This report was prepared for the Aquatic Effects Technology Evaluation (AETE) Program and contains an overview of monitoring issues related to the determination of water quality at very low concentrations.

Recently, improvements in analytical chemistry technology have given scientists the ability to measure lower and lower concentrations of metals and other contaminants in water. Similarly, as the understanding of the environmental effects of contaminants has increased, the acceptable concentrations in water of many of these contaminants have decreased. When monitoring water quality, it is preferable to be able to reliably measure concentrations of contaminants which are one tenth of the acceptable concentrations of those contaminants. Despite improved analytical technology, reliably measuring such low concentrations of contaminants requires great care.

This report outlines methods and quality assurance and quality control practices required to limit or prevent contamination, and ensure the integrity of water samples up to the time of analysis. The report also discusses analytical detection limits, to emphasize that, at very low concentrations, an understanding of the detection limit is essential to interpreting the meaning of water quality analyses. The report also summarizes water quality guidelines and compares guidelines for particular parameters with the detection limits using commercially available analytical technology.

2 Sampling Collection, Preservation and Handling

2.1 Introduction

Data generated for any sample can only be as good as the sample itself. With the increasing ability to detect contaminants in water at lower and lower concentrations, the importance of quality assurance and quality control is increased. The validity of data with very low concentrations of contaminants (i.e., low level data) depends on collecting representative samples and ensuring sample integrity, by taking all necessary steps to ensure that, once collected, samples do not deteriorate and are not contaminated.

Prior to analysis in the laboratory, the integrity of a sample must be maintained during collection, transportation and storage, through the implementation of appropriate quality assurance practices. Possible contamination may be detected and measured through quality control samples.

Sample collection and handling procedures must be documented and must identify:

- the equipment and materials used, including cleaning procedures
- the type of material sampled
- the time and location of sampling
- the person doing the sampling
- all steps in the sample collection/handling process

A precise definition of these aspects is fundamental to ensuring data reliability and becomes very important when the inter-comparability of data is considered. This is particularly true when ultra-trace levels are being measured. Recent findings (Horowitz *et al.* 1996) have focused on the factors that can affect the measured concentrations of dissolved metals, including:

- filter type and diameter
- filtration method (i.e., vacuum or pressure)
- volume of sample processed
- nature of the sample

This is an example of the adage that the method defines the result, and underscores the need for methods to be unambiguously defined and precisely applied so that the result obtained is valid and the data are comparable.

Documented sample collection/handling procedures must contain specifications that ensure that valid results are obtained, including specifications to ensure that:

- samples are not contaminated
- samples do not deteriorate
- there is adequate quality control.

Adequate specifications relating to the above are essential and are particularly critical for testing at ultra-trace levels. Both historical and more recent literature sources have paid particular attention to the role of contamination and the need for "ultra clean" techniques as they relate to sampling, processing and preservation. Initial work in this area focused on marine chemistry (e.g., Bruland 1983). More recent work has focused on freshwater-chemistry and procedures for the decontamination of both equipment and filters (Nriagu *et al.* 1993, 1996).

An overview of quality control practices as they relate to the issues of preservation and contamination are highlighted in the following sections. More complete detail can be found in current procedures published by the various regulatory agencies.

2.2 Water Sample Collection

2.2.1 Options for Water Sample Collection

There are several methods available for the collection of water samples, including:

1) discrete grab samples removed at a particular location at a particular time;
2) composite grab samples which are removed from various locations (usually various depths) at a particular time;
3) composite grab samples which are removed from a particular location at various times; and
4) continuous removal of a sample at a particular location over a selected time interval.

The sampling option used will depend on what is required to collect samples that are representative of the objective of the monitoring. The types of samplers used will depend on the sampling option, but may generally be classified as grab samplers, multiple samplers, and continuous samplers. A brief description of each follows.

Grab samplers: Grab samplers at their most basic level consist of a container that is held just below the surface of the water body being sampled. Other mechanical grab samplers are more sophisticated and provide for sampling at depths of 1 - 2 metres or greater. They include the Van Dorn and Kemmerer samplers. This type of sampler is basically a tube with end seals, a trip mechanism to close these seals and a drain valve. To collect a sample, the tube is lowered, with the end seals raised, by rope to the desired depth. The mechanism that closes the end seals is tripped, the sampler is raised to the surface, and the sample is transferred to a sample bottle.

Grab samplers known as Through Ice Samplers and Flip Samplers or Duncan Samplers have been specially designed to accommodate through-ice sampling.

Multiple Samplers: Multiple samplers are devices that hold more than one bottle. They are used to collect several samples at the same time. The device containing the sample bottles is lowered until all bottle openings are below the surface of the water. The bottles are allowed to fill. The sampler is then pulled out of the water and the bottles are capped.

Continuous Samplers: Automatic samplers that sample (for prescribed intervals) at either fixed or proportional flow rates are available. They use either peristaltic or vacuum pumps.

2.2.2 Techniques for Reduction of Contamination During Sample Collection

Sample collection must be carried out so that any impact on the sample, of the environment surrounding the sample, is minimized.

The location of sampling must be away from areas of natural disturbances which could increase the amount of sediment in a sample (e.g., where wave action disturbs a lake bottom). Equipment touching the bottom of a sampling site can also increase the amount of sediment in a sample.

Care must also be taken to avoid contamination from skin contact with the sample. When collecting grab samples in lakes, hold the sample bottle at arm's length, plunge it below the surface and slowly force it through the water until it is full. This creates a current over the mouth of the bottle such that water entering the bottle will not come in contact with the hand holding it. When sampling from flowing rivers or streams, wade into the river downstream from the sampling site, then upstream until the site is reached. Face upstream, plunge the sample bottle below the surface with the top facing down and then immediately face the bottle top into the current. When the bottle is full, remove it by forcing it into the current and upwards.

When sampling from a boat, care must be taken to reduce contamination from the boat and/or the motor. Collect samples at the bow either with the boat facing into the current or with the boat moving slowly forwards. Hold the bottle at arm's length from the boat, plunge it below the surface and move it slowly into the current. When the bottle is full remove it by forcing it into the current and upwards.

When sampling from a bridge, collect the samples on the upstream side to avoid contamination from the bridge itself or material falling from the bridge. Avoid touching the bridge with any part of the sampling equipment.

Before drilling a hole in ice for sampling, clear loose ice and snow from the area so it does not fall into the hole. Keep the area around the hole clear of dirt, etc. After drilling, remove ice chips and slush from the hole.

Other measures to reduce contamination of samples include:

- do not let anything come in contact with the sample, or the inside of the sample bottle and cap
- keep all sampling equipment clean
- do not smoke in the vicinity of sample collection or handling activities. Smokers should wear

unlined latex or polyethylene gloves.

- sample bottles must be pre-cleaned, capped, and certified by the laboratory
- sample bottles should be opened immediately before sample collection, and closed as soon as possible after sample collection

2.2.3 *In Situ* Monitoring

Most techniques available for the analysis of water samples, such as atomic absorption, do not lend themselves to *in situ* monitoring, since the necessary equipment is not field transportable. An alternative technique that has potential for allowing some *in situ* monitoring is the selective ion electrode (SIE) technique, which could be used to determine free cyanide and undissociated or un-ionized ammonia. However, the detection limits achievable with the SIE technique are not adequate where concentrations are low (Table 1). Detection limits and water quality guidelines are further discussed in Sections 3 and 4.

Table 1: Detection limits achievable for *in situ* monitoring methods, and water quality guidelines for the same parameters (Standards Methods, 19th edition)

Parameter	Guideline	Detection Limit
free cyanide	5 μg/L	50 μg/L
undissociated ammonia	20 μg/L	30 μg/L

Other considerations when using the SIE technique include susceptibility to interference, sensitivity to changes in temperature and ionic strength and slow response times.

These considerations notwithstanding, it is preferable to measure both free cyanide and undissociated (or un-ionized) ammonia *in situ* as opposed to collecting a sample for laboratory analysis if the detection limits are adequate for meeting the objective of monitoring. Once collected, both of these characteristics are unstable. For example, their concentration may be significantly affected by sample aeration, change in temperature and shifts in sample pH; unlike total cyanide and total ammonia they are not amenable to chemical preservation.

2.3 Water Sample Preservation

2.3.1 Methods of Preservation

The objective of water sample preservation is to ensure that samples do not deteriorate or degrade prior to laboratory testing. Chemical preservation, storage temperatures and holding time (i.e., the elapsed time between sampling and testing) all play a key role in sample preservation. Typical sample preservation and storage information are summarized in Table 2, but may vary somewhat for specific methods and jurisdictions.

Table 2: Recommended container types, preservation and storage methods, and holding time for various analytes (Standards Methods, 19th edition; B.C. Environment 1994)

Analyte	Container	Preservation and Storage	Holding Time
Metals, general	P(A); G(A)	For dissolved metals, filter immediately, add HNO_3 to pH < 2	6 months
Mercury	T(A); G(A)	Add H_2SO_4 or HNO_3 to pH < 2, plus $K_2Cr_2O_7$. Refrigerate at 4°C. May also use HCl alone.	28 days
Cyanide	P,G	Add NaOH to pH > 12, refrigerate at 4°C	3 to 14 days, depending on method. 24 hours if sulfide present
Ammonia	P,G	None or add H_2SO_4 to pH < 2, refrigerate at 4°C	28 days, 3 days if no preservation

Notes: P = plastic (polyethylene or equivalent)
G = glass
T = teflon
A = rinsed with 1+1 HNO_3

A source of sample degradation is the sorption of small amounts of metals onto container walls. When measuring very low concentrations of metals, loss to container walls can be significant. The degree to which this occurs will depend on the metal species, concentration, pH, contact time, sample and container composition, presence of dissolved organic carbon and complexing agents (Keith 1991). The addition of nitric acid (HNO_3) usually prevents this from occurring.

A further source of degradation is the formation of salts that precipitate. The most common

occurrence is precipitation of metal oxides and hydroxides due to the reaction of metal ions with oxygen. This precipitation is usually prevented by adding nitric acid: the combination of a low pH (less than 2) and nitrate ions keeps most metal ions in solution. Other acids (especially hydrochloric and sulphuric) may cause precipitation of insoluble salts and/or analytical interferences (Keith 1991).

Water samples containing cyanides may evolve hydrogen cyanide. The addition of sodium hydroxide (NaOH) is used to prevent this. Similarly, water samples containing ammonia may evolve ammonia gas. The addition of sulphuric acid (H_2SO_4) forms stable ammonium sulphate and is used to prevent this.

Storage at 4±2°C slows changes caused by the growth of microorganisms. For example, microbiological activity may be responsible for changes in the nitrate-nitrite-ammonia content (Standard Methods, 19th edition).

Both filtering and the addition of chemical preservatives, where specified, are carried out as soon as possible after samples are collected. Filtering is carried out before adding the chemical preservatives. From sampling until analysis, where specified, samples are kept at 4±2°C. Even when preservation techniques are followed, the shorter the time between sampling and analysis, the more reliable the analytical result. This is particularly true for ultra-low level samples. It is preferable that samples are transported to the laboratory on the day they are collected. Transporting samples in coolers with ice packs is the most common practice for keeping samples at 4±2°C. For ambient temperatures above freezing, samples most likely to deteriorate should be kept closest to the ice packs and enough ice packs should be used to last the duration of the transport time. Although low temperatures reduce biodegradation, freezing can cause degassing, phase separation and container breakage and must be avoided. For extreme ambient temperatures the cooler quality must be adequate to protect the samples from either overheating or freezing.

Holding time is the maximum time that can elapse from sampling to measurement before significant deterioration can be expected to occur.

2.3.2 Monitoring Water Sample Preservation

Preservation should be monitored at several points in the process leading up to the analysis of samples to ensure that the integrity of the samples has not been jeopardized. The following describes actions to be taken at these points. If a nonconformance is identified, it must be recorded and reported. If the decision is to continue with the analysis, the data must be flagged as nonconforming in the report to the client. Corrective action should be taken to identify the cause of the problem and to prevent it from recurring.

Further detail relating to the critical points at which preservation should be monitored appears below.

Collecting samples: Notes on sample preservation should be recorded on or attached to the chain of custody form so that staff involved in the next steps of the process are aware of what has taken place. To be able to monitor whether the time between sampling and analysis falls within the range specified for the analyte of interest, the date (and time) of sampling must be recorded.

Transporting samples from the field to the laboratory: When temperature control of samples is specified, a bottle of reagent water that will not be analysed should be transported with the samples from the field to the laboratory so that the temperature can be checked at the laboratory without contaminating a sample.

Receiving samples in the laboratory: The date (and time) of arrival at the laboratory should be recorded and compared to the date and time of sampling. If the holding time specified for the analyte of interest has been exceeded, the nonconformance must be acted upon. When temperature control is specified, the temperature of the bottle of reagent water sent with the samples must be checked and recorded. If it is outside the acceptable range for the analyte of interest, the nonconformance must be acted upon.

Storing samples in the laboratory prior to analysis: Storage temperatures must be monitored and recorded, preferably daily or using a thermometer that records temperatures continuously. If a

temperature has gone outside the acceptable range, the nonconformance must be acted upon.

Analysing the samples: Just before analysis is carried out, the date (and time) should again be recorded and compared to the date and time of sampling. If the specified sample holding time has been exceeded, the nonconformance must be acted upon.

2.4 Water Sample Contamination

2.4.1 Minimizing Sample Contamination

The six major sources of water sample contamination are:

- sample bottles and caps
- preservatives
- filters
- equipment
- poor sampling, handling and storage practices
- airborne contamination (e.g., dust and fumes)

The following describes practices that help to ensure that contamination is minimized. These practices are essential for all monitoring and are particularly critical for monitoring at ultra-trace levels.

Often more than one organization is involved in the steps of collecting, transporting and storing samples. For example, a laboratory may supply the sampling equipment; an engineering organization may plan and carry out the sampling and transport the samples to the laboratory; and a laboratory may receive and store the samples prior to analysis, but may subcontract part of the work. The project manager must ensure that contamination is minimized in all these steps. This can be partially verified by carrying out both internal and supplier audits.

Both field and laboratory staff need to have relevant qualifications. They must also be trained in the concepts of quality assurance and the technical aspects needed to carry out their roles.

Problems with techniques and practices can be minimized by ensuring instructions related to collecting, transporting and storing samples are well thought out and clearly documented. These documents need to be controlled so that only the current versions are available and in use by field and laboratory staff. Instructions are needed, for example, for the following:

- purchasing supplies (sample bottles and caps, filter paper, equipment)
- purchasing services, including subcontractors
- carrying out ongoing quality control of sample bottles, caps and filter paper, including establishing and using acceptance criteria and acting on nonconformances
- preparing field supplies, including cleaning equipment and sample bottles (where applicable)
- preparing and collecting quality control samples such as travel blanks and field blanks
- shipping field supplies
- labelling sample bottles
- collecting samples
- maintaining records related to sampling
- transporting samples from the field to the laboratory
- receiving samples in the laboratory
- tracking samples in the laboratory
- storing samples in the laboratory
- scheduling analyses
- reporting and recording nonconformances and taking corrective and preventive action.

Details related to minimizing contamination that should be included in these procedures follow.

Sample bottles and caps appropriate for the analytes of interest must be used. They must be checked for contaminant leaching when a supplier is chosen. Ongoing quality control is also needed to ensure the supply continues to be reliable. Standard Methods (19th edition) states that the best sample containers are made of quartz or TFE. Because these containers are expensive, the preferred sample container is made of polypropylene or linear polyethylene with a polyethylene cap. Borosilicate glass containers also may be used, but avoid soft glass containers for samples containing metals in the microgram-per-litre range. Store samples for determination of silver in light-absorbent containers. Use only containers and filters that have been acid rinsed. Standard Methods also states that zinc has been found in black Bakelite-type screw caps. PVC has been reported to contain zinc, iron, antimony, and copper that may leach into water samples, and polyethylene has been reported to contain antimony that may leach into water (Keith 1991). Glass bottles may contaminate samples with boron and/or

silicon (Keith 1991). Glass or teflon bottles must be used for mercury samples and for preservatives to be used in mercury samples, since these materials are impervious to mercury vapour, which can migrate from the atmosphere into acid preservatives and acidified samples.

A storage environment for bottles and caps needs to be such that exposure to dirt, dust and fumes is minimized. Bottles should be capped before they are sent to the field, opened just before sampling and capped immediately and tightly following sampling to minimize the time the sample/preservative is exposed to the atmosphere. During sampling, caps must be protected from contamination. It is recommended that all bottles be pre-cleaned, capped and tested in the laboratory. If not pre-cleaned, the bottles should be triple rinsed in the water to be sampled, although this may lead to a build-up of contaminants in turbid water.

Chemicals used as preservatives must be high (ultra) purity. They are usually obtained commercially. The containers for these chemicals need to be labelled with expiry dates to help ensure their integrity. The environment where chemical preservatives are added to sample bottles needs to be such that exposure to dirt, dust and fumes is minimized. Lead contamination from dust and fumes is particularly a problem. To minimize contamination from the field environment, chemical preservatives may be prepackaged in single sample aliquots. It is critical that quantities of chemicals added as preservatives are controlled to obtain reproducible blanks. The amount of preservative required to reach a specified pH should be determined by titration on water samples collected specifically for that purpose. The amount of preservative needed should never be arrived at by measuring the pH of the actual sample.

As with sample bottles and caps, filter papers must be checked for contaminant leaching when a supplier is chosen. Ongoing quality control must also be carried out.

Equipment such as samplers and filter units must be checked as possible sources of contamination before being put into use. Stainless steel containers may contribute to chromium, iron, nickel and molybdenum contamination (Keith 1991). Before filter units go to the field, they should be acid washed and soaked in reagent water. In the field, they should be rinsed at least twice with reagent

water between samples to prevent carry-over. Zinc has been found in many rubber and plastic products (Standard Methods, 19th edition). Plastic pipette tips are often contaminated with copper, iron, zinc, and cadmium; before use soak in 2N HCl or HNO_3 for several days and rinse with deionized water (Standard Methods, 19th edition). Disposable gloves can also be a source of zinc contamination.

Coolers must be kept clean. Ice packs should be used in coolers rather than ice since ice can be expected to melt during the transport of samples and the resulting water may contaminate the samples.

Basic good practices in sampling include having clean hands and never touching the insides of sample bottles or caps with anything other than the sample itself and the preservative. Sampling must be carried out in a manner that prevents contamination from the surrounding environment. There must be no smoking in the vicinity of sample collection and handling activities, and smokers should wear unlined latex or polyethylene gloves. When samples arrive at the laboratory they need to be stored separately from standards and reagents to prevent the possibility of cross contamination. Notes on conditions that could affect the integrity of the data should always be kept on or with the chain of custody form so that staff involved in the next steps of the process are aware of what has occurred.

2.4.2 Monitoring Sample Contamination

The use of blanks to monitor sample contamination is extremely important. Reagent water substitutes for the sample in such blanks and the source of the reagent water must be monitored to ensure it is free from contaminants. Records should be kept of these results.

Generally, blanks should contain no measurable contamination. Where some contamination is detected, it is possible that this contamination is related to the sampling method, although other possibilities should be ruled out. In order to respond to contaminated blanks, acceptance criteria, also

called nonconformance criteria, must be established and documented for each type of blank. Analysts use these criteria to identify data that are unreliable because of unacceptable levels of contamination.

If a result for a blank is outside the acceptance criteria, the nonconformance must be recorded and reported. If the decision is to continue with the analysis, the data must be flagged as nonconforming in the report to the client. Corrective action should be taken to identify the cause of the problem and to prevent it from recurring.

Data for sampling blanks should be reported with the data for the samples.

The main types of blanks are discussed below.

Trip Blanks:

- Trip blanks are also referred to as travel or transport blanks.
- Trip blanks are used to check contamination from sample bottles, caps and preservatives during transport, storage and analysis.
- At least one trip blank should be submitted with each batch of samples.
- A sample bottle is filled in the laboratory with reagent water and preserved in the same manner as the samples will be.
- Trip blanks are transported to the field with the regular sample bottles and submitted unopened with the samples to the laboratory.
- They are opened at the time of analysis and the contents are analyzed in the same manner as the samples.

Field Blanks:

- Field blanks are also referred to as site blanks.
- Field blanks are used to check contamination from all the potential sources of contamination of the sample. These include possible contamination from sample bottles, caps, preservatives, equipment, filter paper, the atmospheric environment in the field, sampling techniques, and analysis.
- At least one field blank should be collected per day per collection apparatus.
- Reagent water is transported to the field and carried through all sample handling/processing steps that the test samples undergo (e.g., filtration, transfer to a sample container, chemical preservation, exposure to the atmosphere).
- Field blanks are transported, stored and analyzed in the same manner as the samples.

If a field blank identifies a contamination problem, the trip blank can be used to help isolate the

source(s). Further isolation of the source can also be supplied by what are known as equipment blanks and filtration blanks.

Equipment Blanks:

- Equipment blanks are also referred to as rinseate blanks.
- Equipment blanks are used to check contamination from sampling equipment.
- The equipment is rinsed with reagent water that is collected in a clean sample bottle.
- Equipment blanks are preserved and analyzed in the same manner as the samples.

Filtration Blanks:

- Filtration blanks are used to check contamination from the filtering apparatus and the filter paper.
- They are collected both at the start and at some point during sample collection.
- Filtration blanks are prepared using reagent water that is filtered in the same manner as the samples.
- Filtration blanks are preserved and analyzed in the same manner as the samples.

The analysis of field replicate samples and reference samples of known concentration can also be used to monitor sample contamination. Wide variations in replicate results and reference sample recoveries exceeding 100% may be indicative of sample contamination.

3 Analytical Detection Limits

3.1 Introduction

Once samples reach the laboratory, a key consideration in the interpretation of analytical results for samples with very low concentrations of contaminants is the detection limit. All analytical systems, such as those used to determine metal concentrations in water, have limiting low concentrations, or detection limits, below which a particular analyte cannot be detected.

At its most basic level an analytical system is a systematic process used to generate test data. For example, an inductively-coupled plasma – mass spectrometry (ICP-MS) analysis, together with associated sample preparation procedures, is an analytical system which can be used to measure metal concentrations in water. The system is usually described by a test method which will identify three key elements of any analytical system:

- the analytical technique used
- the test material
- each step in the testing process

Each of these elements will influence the detection limit. Some analytical techniques have greater sensitivity than others, which will influence detection limit capability. The nature of the test material, and in particular the nature of the sample matrix at the point of measurement, can also affect analyte response and the detection limit (see Section 3.4). The first two elements (the analytical technique used and the test material) are intimately related to the third element (each step in the testing process).

Random measurement error (measurement uncertainty) associated with the analytical system, under the conditions of low (or zero) concentration, define the detection limit. The relationship between measurement uncertainty and the detection limit, as well as calculation methods, are further discussed in Appendix 1. The measurement uncertainty is expressed in terms of a standard deviation, based on replicate analysis of identical samples. Appropriate replicate analysis of identical samples will include

within run data, and duplicate data from successive runs.

3.2 Types of Detection Limits

3.2.1 Method Detection Limit and Reliable Detection Limit

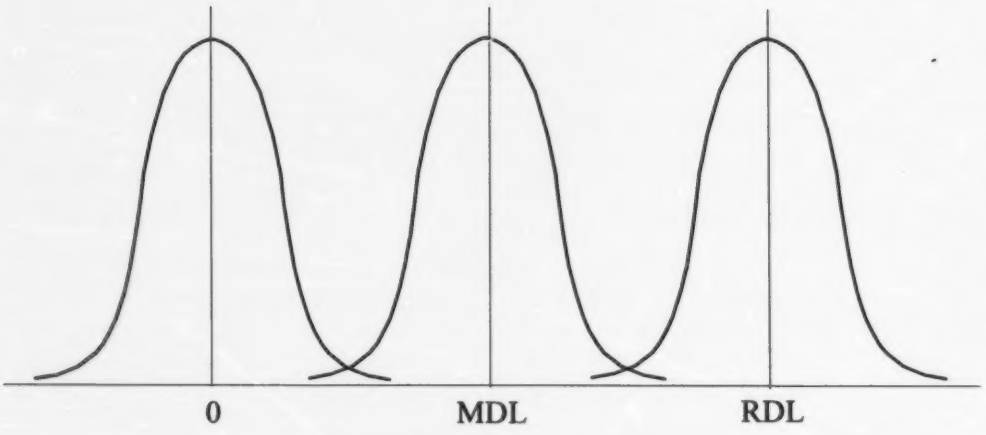
There are two distinct detection limits that may be reported - the **Method Detection Limit** (MDL) and the **Reliable Detection Limit** (RDL). Methods for calculating the detection limit are described in Appendix 1. The MDL and RDL may be defined as follows:

Method Detection Limit (MDL): the measured response at which there is a stated probability (usually 95 or 99%) that the analyte is present. The MDL may be expressed as 1.64σ and 2.33σ, respectively, at 95 and 99% probability where σ is the population standard deviation.

Reliable Detection Limit (RDL): the lowest analyte concentration required to be present in the sample to ensure detection; i.e., the analytical response that will exceed the MDL with stated probability (usually 95 or 99%). The RDL may be expressed as $2(1.64)\sigma$ and $2(2.33)\sigma$, respectively, at 95 and 99% probability where σ is the population standard deviation.

It is important to note that, of the various detection limits in use, the one that is in most common usage and best approximates an industry-standard is the MDL (99%). In the absence of other qualifiers it is usually safe to assume a reported detection limit is the MDL (99%).

Note that the RDL is twice the MDL for a given confidence interval. This multiplier of 2 is determined statistically, and provides the assured level of confidence that data which exceed the RDL are statistically significant. The relationship between these detection limits is illustrated in the following figure:



The Reliable Detection Limit (RDL) represents:

- the smallest analyte concentration at which there is a specific probability of detection
- the smallest analyte concentration which is statistically significant
- the point at which a measured value becomes believable

3.3.2 Limit of Quantification

Another limit, the **Limit of Quantitation** or LOQ[1], provides an assured level of confidence that data which exceed it are statistically significant. Table 3 presents a comparison of the MDL, RDL and LOQ.

[1] The USEPA, at times, uses the terminology Minimum Level or ML when referring to the LOQ

Table 3: Comparison of the Method Detection Limit (MDL), Reliable Detection Limit (RDL) and Limit of Quantitation (LOQ), determined for a sample size of n=7, and using the standard deviation (s) of a low, but statistically significant analyte concentration.

Limit Name	Limit Value (n=7)		Multiplier
	99% C.I.	95% C.I.	
MDL	3.14s	1.94s	1
RDL	6.28s	3.88s	2
LOQ	10s	[6.17s]*	3.18**

*The LOQ was originally defined at the 99% C.I. The value for the 95% C.I. is not an LOQ and appears only for the purposes of comparison.
**The multiplier of 3.18 used for the LOQ has been arbitrarily selected

3.3.3 Consensus Detection Limit

The application of a specific test method always has distinguishing features, such as differences in personnel, technique, equipment and environment, which are unique to a particular laboratory. These differences combine to produce variations in the application of a test method, and by extension variations in the detection limits provided by different laboratories. The **consensus detection limit** includes the between-laboratory source of variability.

Inter-laboratory comparison studies using duplicate samples at multiple concentrations can be used to calculate an inter-laboratory precision function and by extension a consensus detection limit.

The precision function defines the relation between standard deviation and concentration; extrapolation of the precision function to zero concentration will provide a standard deviation which can be used in the calculation of a consensus detection limit.

Consensus detection limits are representative of the particular test method or technology and it could be argued that, as such, they are the most suitable choice of detection limit for (establishing and) interpreting regulatory requirements. Further, since confidence intervals may be assigned to consensus detection limits they also provide a useful benchmark for evaluating the performance of individual

laboratories. For example, if the detection limit provided by an individual laboratory exceeds the limit specified by the chosen confidence interval (e.g., 95%), it can be assumed that that particular laboratory has contributing sources of variability that are outside the norm.

3.4 Interpreting Low Level Data

An understanding of the meaning and significance of the different detection limits described above can aid in the interpretation of low level data, such as very low concentrations of metal in water. Guidelines for the statistical interpretation of low level data are summarized in Table 4. Further information on the statistical interpretation of low level data is given in Appendix 2.

Table 4: Guidelines for interpreting low level data

Observed Test Result	Interpretation
Result < MDL	analyte not detected
MDL ≤ Result < RDL	analyte is present (e.g., 95 or 99% probability), but result is not statistically significant; i.e., an uncertainty cannot be assigned
RDL ≤ Result < LOQ	result is borderline statistically significant at the RDL (e.g., 95 or 99% C.I.); % relative uncertainty (e.g., 95 or 99% C.I.) of reported result will be on an interval below ± 100%
Result ≥ LOQ	result is statistically significant at the LOQ; % relative uncertainty (e.g., 95 or 99% C.I.) will likely be on an interval below approximately ± 50%

Notes: (1) RDL = 2 x MDL and LOQ = 3.18 x MDL
(2) The MDL and RDL may be reported at either the 95 or 99% probability level. Depending on the choice, the RDL will be borderline statistically significant at the 95 or 99% probability level.
(3) Many laboratories use the MDL (99% probability) as a reporting detection limit, as cited by the USEPA and the Province of Ontario. In some cases (e.g., some effluents) the USEPA specifies using the equivalent of the LOQ as the reporting detection limit.
(4) The % relative uncertainty will depend on the probability level chosen (e.g., 95 or 99%). See below for examples.
(5) When identical test samples are analyzed in replicate and the results averaged, the % relative uncertainty will be reduced by a factor of $\sqrt{n}$ where n is the number of replicate samples.

3.5 Influence of the Sample Matrix on the Detection Limit

It was stated in Section 3.2 that the nature of the test material, and in particular the sample matrix at the point of measurement, can affect analyte response and the detection limit. When detection limits are referenced to reagent water, matrices different from reagent water can degrade the detection limit in two ways:

- by decreasing analytical response
- by increasing variability in analyte recovery.

These cause and effect relationships are shown in Table 5.

Table 5: Relationships between sample matrix and effects on detection limits

Cause	Possible Effect
matrix difference relative to reagent water	increased variability or uncertainty in analyte recovery*
matrix difference, relative to reagent water, at the point of measurement	reduced analytical response

* analyte recovery refers to the analyte available for measurement subsequent to sample preparation.

Table 6 considers selected parameter groupings and highlights:

- sample preparation, which can increase variability, relative to reagent water
- matrix differences at the point of measurement, which can influence analytical response.

The matrix difference at the point of measurement may vary significantly and will depend on the sample preparation. In the absence of materials known to interfere, a matrix (i.e., dissolved solids) burden of up to 0.1%, (including extreme water hardness), will not normally affect the detection limit for the relevant analytical techniques (e.g., atomic absorption, or inductively coupled plasma). The USEPA (1994) stated that "waste water of high quality will have very little matrix interference". However, when interfering materials are suspected their presence can be verified by using a method known as standard additions. In the event interferences are verified, the options are to:

- estimate the detection limit using samples (and calibration standards) which have the same matrix as the test samples, or
- preferably, use an alternate detection system which is not influenced by the interference.

Table 6: Comparison of selected parameter groupings, sample preparation and matrix differences

Parameter Grouping	Sample Preparation	Matrix Difference
Dissolved Metals (Ag, Al, As, Cr, Cd, Cu, Fe, Mn, Mo, Ni, Sb, Se, Zn)	filtration	filtered materials other than the analyte of interest
Total Metals	digestion plus filtration	digested and filtered materials other than the analytes of interest
Mercury	(filtration plus) digestion plus cold vapour generation	negligible
Metal Hydrides (As, Sb, Se,)	(filtration plus) digestion plus hydride generation	volatile materials including metal hydrides other than the analyte of interest.
Cyanide	pH adjustment plus distillation	negligible
Ammonia	pH adjustment	original materials other than the analyte of interest

3.6 Reporting and Quality Control

1) The detection limit reported by the laboratory should meet client needs and should be appropriately identified (e.g., MDL, RDL or LOQ at a prescribed probability level).

2) The laboratory should provide estimates of measurement uncertainty (e.g., test method precision function) as required by the client.

3) The reported detection limit and estimates of measurement uncertainty should be validated periodically and should be based upon appropriate calculation of the standard deviation.

4) The laboratory should ensure that the test method is producing test results which are both traceable and in statistical control.

5) All validation and quality control data should be available for audit (i.e., by either the client or for the purposes of laboratory accreditation).

4 Water Quality Guidelines and Achievable Detection Limits

4.1 Overview of Water Quality Guidelines

Table 7 summarizes water quality guidelines for the protection of aquatic life from the Province of Ontario, the Province of British Columbia, the Canadian Council of Ministers of the Environment (CCME) and the USEPA. Where guidelines for chronic exposure or interim guidelines are available these guidelines are quoted since they are the more stringent.

In Section 4.3 the guidelines in Table 7 are compared with detection limits that are achievable using existing technology.

4.2 Achievable Detection Limits

A summary of achievable detection limits using existing analytical methods is presented in Table 8. The CAEAL[2] detection limits are based on a survey of the detection limits used by laboratories participating in the SCC - CAEAL accreditation program. Information was available for approximately 60 laboratories and the varying number of laboratory responses depended, in part, on:

- the degree to which the various test methods are in use, and
- the subset of the 60 labs for which information was available.

A summary of laboratory responses by parameter group and test method is in Appendix 3.

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[2] CAEAL is the Canadian Association of Environmental and Analytical Laboratories
SCC is the Standards Council of Canada

Table 7: Summary of water quality guidelines for selected parameters

Parameter	CCME		British Columbia		Ontario		USEPA
	variable	guidelines µg/L	variable	guidelines µg/L	variable	guidelines µg/L	guidelines µg/L
Al	pH < 6.5 pH ≥ 6.5	5100	pH 6.5 pH 6.5	F 50	pH 4.5 – 5.5 pH > 5.5 – 6.5 pH > 6.5 – 9.0	15* B 75*	—
Sb		—		20*		20*	30
As		5*		50		5*	190
Cd	30 mg/L H 90 mg/L H 150 mg/L H 210 mg/L H	0.01 0.03 0.05 0.06	30 mg/L H 90 mg/L H 150 mg/L H 210 mg/L H	0.01 0.03 0.05 0.06	0–100 mg/L H > 100 mg/L H	0.1* 0.5*	1.1*
Cr		2** 20***		2** 20***		100	11
Cu	0–60 mg/L H 60–120 mg/L H 120–180 mg/L H > 180 mg/L H	2234	0–50 mg/L H > 50 mg/L H	2 F	0–20 mg/L H > 20 mg/L H	15	12+
Fe		300		300		300	1000
Pb	0–60 mg/L H 60–120 mg/L H 120–180 mg/L H > 180 mg/L H	1247	0–8 mg/L H > 8 mg/L H	3 F	0–30 mg/L H 30–80 mg/L H > 80 mg/L H	1* 3* 5*	3.2+
Mn		—		100 (50 for drinking water)		—	—
Hg		0.1		0.02		0.2	0.012
Mo		—		1000 (10 for irrigation)		10*	—
Ni	0–60 mg/L H 60–120 mg/L H 120–180 mg/L H > 180 mg/L H	25 65 110 150	0–60 mg/L H 60–120 mg/L H 120–180 mg/L H > 180 mg/L H	25 65 110 150		25	160+
Se		1		1		100	5
Ag		0.1		0.05		0.1	0.12
Zn		30*		30*		20*	110+
Ammonia (total)	pH 6.5, 10°C pH 8.0, 10°C	2200 1370	pH 8.5, 20°C pH 9.0, 20°C	261 102		—	—
Ammonia (undiss.)		—		—		20	—
Cyanide (free)		5		—		5	5.2
Cyanide (WAD)		—		5		—	—

Notes:

Metals guidelines are for total metals

* = interim, proposed or tentative value

** = value for protection of aquatic communities

*** = value for protection of fish

F = value calculated by formula

B = value based on background levels

H = Hardness as $CaCO_3$

+ = hardness dependent guidelines (100 mg/L H used)

Cyanide (free) and ammonia (undissociated), ideally, require *in situ* monitoring.

Table 8: Summary of achievable detection limits

Parameter	Method	Detection Limit, µg/L (1)		
		SM or USEPA (4)	CAEAL (5)	NLET (6) (except as noted)
Aluminum	AA Flame	100	50	
	ICP	40	50	
	AA Graphite	3	5	
	ICP-MS	0.05	0.5	
Antimony	AA Flame	70	-	
	ICP	30	-	
	AA-Hydride	2	2	
	AA Graphite	3	1	
	ICP-MS	0.08	0.1	
Arsenic	AA Flame	-	-	
	ICP	50	-	
	AA-Hydride	2	2	
	AA Graphite	1	1	
	ICP-MS	0.9	1	
	ICP-Hydride			0.1
Cadmium	AA Flame	2	2	
	ICP	4	3	
	AA Graphite	0.1	0.2	
	ICP-MS	0.1	0.05	0.005
Chromium	AA Flame	20	20	
	ICP	7	5	
	AA Graphite	2	1	
	ICP-MS	0.07	0.05	
Copper	AA Flame	10	10	
	ICP	6	5	
	AA Graphite	1	1	
	ICP-MS	0.03	0.02	
Iron	AA Flame	20	20	
	ICP	7	10	
	AA Graphite	1	5	
	ICP-MS	-	6	
Lead	AA Flame	50	302010.05	
	ICP	40		
	AA Graphite	1		
	ICP-MS	0.08		
Manganese	AA Flame	10	10	
	ICP	2	5	
	AA Graphite	0.2	1	
	ICP-MS	0.1	0.05	
Mercury	AA cold vapour	0.2	0.05	0.005 (7)
Molybdenum	AA Flame	100	-	
	ICP	8	10	
	AA Graphite	1	1	
	ICP-MS	0.1	0.1	

Table 8: Summary of achievable detection limits (continued)

Parameter	Method	Detection Limit, µg/L (1)		
		SM or USEPA (4)	CAEAL (5)	NLET (6) (except as noted)
Nickel	AA Flame	20	20	
	ICP	15	10	
	AA Graphite	1	1	
	ICP-MS	0.02	0.2	
Selenium	AA Flame	-	-	
	ICP	75	-	
	AA-Hydride	2	2	
	AA Graphite	2	1	
	ICP-MS	5	1	
	ICP-Hydride			0.1
Silver	AA Flame	10	-	
	ICP	7	-	
	AA Graphite	0.2	0.1	
	ICP-MS	0.05	0.05	0.005
Zinc	AA Flame	5	10	
	ICP	2	5	
	AA Graphite	0.5	0.5	
	ICP-MS	0.2	0.2	
Ammonia (2)	Colorimetric	-	5	
Cyanide (3)	Colorimetric	-	4	0.5 (8)

Notes:

1) The detection limits for metals (mercury excepted) are for dissolved metals.
2) The detection limit for ammonia is for total ammonia.
3) The detection limit for cyanide is for total (and WAD) cyanide.
4) SM or USEPA Detection Limits - in the absence of a value quoted by Standard Methods, a USEPA value is used. It can probably be assumed that the Standard Methods and USEPA detection limits approximate the MDL (99% probability).
5) The CAEAL detection limits identified as achievable detection limits are the median detection limits provided by the CAEAL laboratories. As such, they can be considered to approximate a best estimate of consensus detection limits for the Canadian laboratory industry. The approach used by Canadian laboratories to calculate reporting detection limits is not necessarily uniform. However, it is probably safe to assume that the detection limit reported by a majority of the laboratories will approximate the MDL (99% probability). This means that the quoted CAEAL detection limits approximate the MDL (99%).
6) National Laboratory for Environmental Testing, Environment Canada. Burlington, Ontario Detection limits listed only for those parameters from Table 10 which cannot achieve a detection limit 1/10 of the water quality guideline using technology widely used commercially.
7) Analytical Service Laboratories (ASL) Ltd, Vancouver, B.C.
8) Pacific Environmental Science Centre, Environment Canada. North Vancouver, B.C.

4.3 Comparison of Detection Limits and Water Quality Guidelines

In Table 9 water quality guidelines are compared[3] with test methods that have method detection limits[4] which are equal to or less than the guideline value. Since it is preferable to have a detection limit which is significantly less than the water quality guideline, a 1:10 MDL:WQC ratio is applied and the test methods which achieve this ratio are identified by a star (*). In many cases a 1:10 MDL:WQC ratio is not generally achievable using the test methods identified. These cases are summarized in Table 10.

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[3] For the metals, the water quality guidelines specify total metals and the achievable detection limits are based on dissolved metals. So, in the strictest sense, they are not directly comparable; i.e., digestion steps associated with total metals will introduce additional variability into the test method and by extension will tend to increase the detection limit. In the discussion in this section it is assumed that the detection limits are interchangeable. However, the distinction that is noted above should be kept in mind.

[4] Since the achievable detection limits in Table 8 are based on the MDL (99%) they need to be multiplied by a factor of at least 2 before they can be considered statistically significant (see Table 3).

Table 9: Comparison of water quality guidelines with analytical methods that have method detection limits which are equal to or less than the guideline value

Parameter	Guideline, µg/L	Applicable Methods
Aluminum	505	AA Flame, ICP, AA Graphite*, ICP-MS* AA Graphite, ICP-MS*
Antimony	20	AA Hydrie*, AA Graphite, ICP-MS*
Arsenic	5	AA Hydride, AA Graphite, ICP-MS
Cadmium	0.06 0.01	ICP-MS none
Chromium	202	AA Flame, ICP, AA Graphite*, ICP-MS* AA Graphite, ICP-MS*
Copper	42	AA Graphite, ICP-MS* AA Graphite, ICP-MS*
Iron	300	AA Flame*, ICP*, AA Graphite*, ICP-MS*
Lead	71	AA Graphite, ICP-MS* AA Graphite, ICP-MS
Manganese	100 (50**)	AA Flame*, ICP*, AA Graphite*, ICP-MS*
Mercury	0.1 0.02 (BC)	AA Cold Vapour none
Molybdenum	10***	ICP, AA Graphite*, ICP-MS*
Nickel	15025	AA Flame, ICP*, AA Graphite*, ICP-MS* AA Flame, ICP, AA Graphite*, ICP-MS*
Selenium	1	AA Hydride, AA Graphite, ICP-MS
Silver	0.1 0.05 (BC)	AA Graphite, ICP-MS ICP-MS
Zinc	20	AA Flame, ICP, AA Graphite*, ICP-MS*
Ammonia	102	Colorimetric*
Cyanide	5	Colorimetric

Notes:

1) Guideline - the values (or ranges) used are the lowest quoted in Canadian sources (i.e., CCME, B.C. and Ontario)
2) Applicable Methods are referenced to CAEAL detection limits.
3) * Method Detection Limit is at least 1/10 of guideline
4) ** drinking water guideline
5) *** guideline for use in irrigation

Table 10: Summary of parameters for which a method detection limit (MDL) at least ten times lower than the water quality guideline (WQC) is not currently achievable

Parameter	Guideline, µg/L	MDL:WQC Ratio	Best Available Ratio*
Arsenic	5	1:5	1:10
Cadmium	0.06	1:1	1:10
Cadmium	0.01	**	1:2
Mercury	0.1	1:2	1:20
Mercury	0.02	**	1:4
Selenium	1	1:1	1:10
Silver	0.1	1:2	1:20
Silver	0.05	1:1	1:10
Cyanide	5	1:1	1:10

Notes:

* ratios calculated using best technology available in Canada, including detection limits at NLET (see Table 8). These ratios may not be commercially available at this time.

** WQC < MDL

When comparing analytical results with water quality guidelines, interpretation needs to be done with care because as the MDL:WQC or MDL:Result ratio is lowered the measurement uncertainty increases. Beyond a ratio of approximately 1:2 the data are no longer statistically significant, since the data fall between the MDL and the RDL (see Table 4).

Table 11: Comparison of measurement uncertainty at different MDL:Result ratios, using copper data from the sample calculation in Appendix 1

MDL:Result	Measurement Uncertainty (99% C.I.)
1:10	± 21.4%
1:5	± 32.9%
1:3	± 48.2%
1:2	± 67.4%
1:1	analyte detected but result is not statistically significant

Notes:

(1) MDL = 0.010 mg/L

(2) Results below 2 x MDL = RDL (i.e., 0.020 mg/L in this case) should not be reported for compliance purposes.

The comparison in Table 11 illustrates how measurement uncertainty increases as concentration decreases. At the limit of statistical significance where the concentration is 2 x MDL (i.e., 0.020 mg/l), a reported analytical result will have a measurement uncertainty of ± 67.4% and should be expressed as 0.020 ± 0.014 mg/l. This means, for the copper example, that there is a 99% probability that the actual concentration of the sample lies on the interval 0.020 ± 0.014 mg/l. Thus, comparison of water quality guidelines with analytical data needs to not only consider the observed value, but also the confidence interval associated with that value.

Clearly, verifying that water quality guidelines have been met can become very complicated when the guidelines are set at or near the analytical limit of detection. This complication needs to be recognized by regulators and adequate guidelines identified.

Where appropriate, such guidelines could include a requirement to base reported results on the analysis of replicate samples, because averaging the results of n replicate samples reduces the measurement uncertainty by a factor of $\sqrt{n}$ (see Table 12).

Table 12: The impact of replicate samples on measurement uncertainty, using data from the sample calculation in Appendix 1.

MDL:Result	Measurement Uncertainty (99% C.I.)				
	n = 1	n = 2	n = 3	n = 5	n = 10
1:10	21.4	15.1	12.4	9.6	6.8
1:5	32.9	23.3	19	14.7	10.4
1:3	48.2	34.1	27.8	21.6	15.2
1:2	67.4	47.7	38.9	30.1	21.3

When a MDL:Result (or MDL:WQC) ratio of 1:10 is achieved there is a measurement uncertainty of approximately ± 20% (i.e., for n = 1). As the MDL:WQC ratio is lowered n must increase if the approximate uncertainty of ±20% is to be maintained (see the underlined values in Table 12). At a MDL:WQC ratio of 1:1 the analyte is detected, but the result is no longer statistically significant and an uncertainty cannot be assigned.

5 Considerations for the Selection of a Laboratory

Clients need to have confidence in the quality of the data reported by a laboratory. In Canada, laboratories which are accredited by the SCC - CAEAL program will have been audited for compliance with the following standards.

- ISO Guide 25; General Requirements for the Competence of Testing Laboratories, 1990.
- CAN/CSA Z753; Requirements for the Competence of Environmental Laboratories, A National Standard of Canada, 1995.

Included in these standards are requirements related to personnel, accommodation and environment, work instructions, records, document control, procurement, equipment, quality audits, nonconformances, corrective action and preventive action. Laboratories that are accredited under these standards can be expected to be familiar with the concepts of quality assurance and to have systems in place for maintaining records related to quality control and quality assurance.

Accredited laboratories also participate in performance evaluation (i.e., inter-laboratory comparison) studies for selected tests. Clients choosing an accredited laboratory may ask to see the laboratory's performance evaluation records as well as audit reports prepared by the accrediting body.

In addition, it is often prudent for the client to conduct a supplier audit of the laboratory, with emphasis on the particular tests for which the laboratory will be supplying test results. Such an audit could include the following points:

- check that procedures for collecting, transporting and storing samples are documented as described in Section 2.4.1
- examine the system for quality control of sample bottles, caps, filter papers and chemical preservatives; check associated records
- check storage areas and temperature records to ensure appropriate temperatures have been maintained
- examine the system for checking the time lapse between sampling and analysis; check associated records of nonconformances
- check analyst training records
- check records of reagent water quality

- check records of audits carried out internally for the laboratory
- check records of performance (proficiency) testing for the analytes of interest
- examine the documented procedures for method validation, in particular to gain an understanding of how detection limits are defined and determined
- check the validation records for detection limit, precision and accuracy for the analytes of interest
- examine the test methods for the analytes of interest to ensure they include reference details on:
  - sample history requirements (e.g., field filtration, chemical preservation, storage conditions, holding time)
  - quality control samples (e.g., blanks, replicates, reference materials) to be analyzed
  - acceptance criteria for results from quality control samples, including trip or field blanks
- check records of method nonconformances for the analytes of interest
- examine the provision for including flags for nonconforming results in test reports
- check how detection limits reported to clients for the analytes of interest relate to detection limits documented with the method validation material (i.e., clarify if the detection limits are MDL's, RDL's, or LOQ's as described in Section 3, or none of these)
- interview analysts carrying out analysis for the analytes of interest to ascertain if they are familiar with and following documented test methods

Laboratories should be notified in advance of supplier audits. As part of the auditing process, these audits should include a report to the audited laboratory before the auditor leaves the laboratory. This ensures the laboratory understands problems or needs identified by the auditor and has the opportunity to address deficiencies. It is also part of the audit process for the auditor to request evidence from the laboratory, within a reasonable time period, that problems have been rectified. Audit reports and responses should be kept on file by the client as a record of supplier capability.

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Appendix 1: Detection Limit Calculation

A detection limit for an analytical system is a statistically determined characteristic of that system. The detection limit is ultimately defined by random errors associated with the testing process, under the conditions of zero (or low) concentrations. This relationship between random measurement error, more commonly referred to as measurement uncertainty, and the detection limit, is further discussed below.

In practice the measurement uncertainty is expressed in terms of a standard deviation, based on replicate analysis of identical samples, where:

- the test samples have undergone all sample processing steps specified in the test method, and
- the test results have been calculated using the calculation routines specified by the test method.

Note that the calculation routines include the combination of individual and/or blank results used to produce the final test result.

Appropriate replicate analysis of identical samples will include:

- within run data
- duplicate data from successive runs

The expressions used to calculate the standard deviation are summarized in Table A.1

Table A.1: Calculation of standard deviation

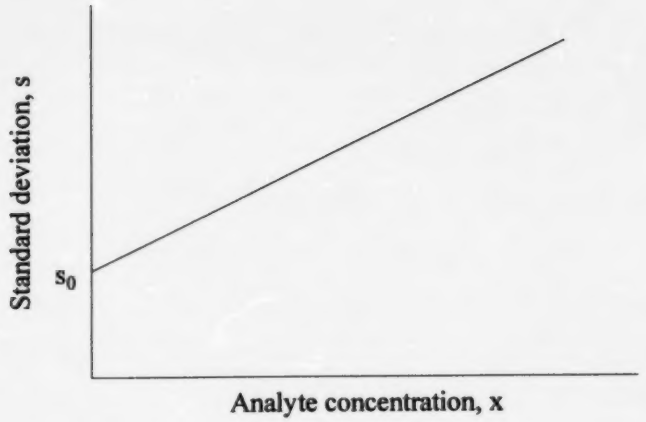
Type of data	Standard Deviation Calculation
within run data	$s = \sqrt{\Sigma(x_i - \bar{x})^2/(n-1)}$
duplicate data	$s = \left[\Sigma\lvert x_1 - x_2\rvert^2/2n\right]^{1/2}$ or $s = \left[\Sigma\lvert x_1 - x_2\rvert/n\right]/1.13$

An additional factor that influences the standard deviation is the concentration of the analyte, and the relation defining the dependence of the standard deviation on analyte concentration, x, for a particular test method is known as the precision function:

$$s = mx + s_0$$

where: s = standard deviation
m = ?
x = analyte concentration
s_0 = standard deviation at zero concentration

The precision function for a particular analyte and test method may be represented graphically as follows:



A plot of standard deviation (s) versus analyte concentrations (x) should be obtained from at least 3 to 5 samples having appropriate concentrations. Note that the respective values of s and x should be based on an equivalent number of at least n = 7 determinations.

The precision function has two important applications:

- estimating the measurement uncertainty, at a specified confidence level (e.g., 95 or 99%), of a reported test result
- providing a limiting standard deviation, s_0, at zero concentration which can be used to estimate the detection limit

Once the measurement uncertainty and precision function are known, the detection limit can be calculated. The detection limit associated with a test method is related to the measurement uncertainty at zero (or low) concentration. There are two ways to obtain such an uncertainty:

- use the standard deviation, s_0, extrapolated to zero concentration, or
- use the standard deviation, s, provided by a low, but statistically significant, analyte concentration

Note that both s_0 and s should be based on at least n = 7 determinations. Once the standard deviation has been obtained, the following procedure is used to determine the detection limit:

1) use a standard deviation based on within run and/or duplicate data
2) identify the standard deviation (i.e., s_0 or s) and the corresponding degrees of freedom (e.g., n-1)
3) identify the desired confidence level (e.g., 95 or 99%) and appropriate t-statistic (one sided test)

4) apply the following calculations, as appropriate; MDL = ts or ts_0 and RDL = 2ts or $2ts_0$.

These steps are illustrated in the following sample calculations, for dissolved copper in water, analysed by flame AA. The example assumes that the precision function is s = 0.032x + 0.0037 with n = 12 (i.e., the results for s and x used to plot the curve have been determined using n = 12 determinations). The example calculations follow.

1. Detection Limit Calculation

n = 12, s_0 = 0.0037	**Result**	
	99% C.I. (t = 2.70)	**95% C.I. (t = 1.80)**
MDL = ts_0	0.010 mg/L	0.0067 mg/L
RDL = 2MDL	0.020 mg/L	0.013 mg/L
LOQ = 3.18 MDL	0.032 mg/L	[0.021 mg/L]

2. Uncertainty Calculation

n = 12; s = 0.032 x + 0.0037 **t = 3.11 (99% C.I.)** **t = 2.20 (95% C.I.)**	**Result**			
	Uncertainty = ± ts		**% Rel. Uncertainty = ± 100ts/x**	
	99%	**95%**	**99%**	**95%**
X = RDL (95%) = 0.013	0.0128	0.0091	98.7%	70.0%
X = RDL (99%) = 0.020	0.0134	0.0095	67.0%	47.5%
X = LOQ (99%) = 0.032	0.0147	0.0104	47.0%	32.5%

Appendix 2: Considerations in Interpretation of Low Level Data

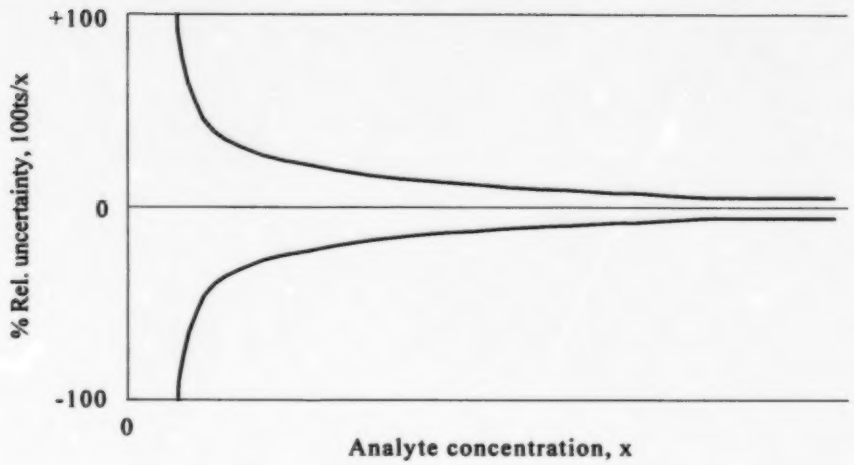
When interpreting low level data the questions that present themselves are the following:

1) Does the test result identify the analyte as being present in the sample?
2) If so, is the result statistically significant (i.e., is it possible to assign a measurement uncertainty to the test result)?
3) And finally, if the test result is statistically significant, what is its measurement uncertainty?

A knowledge of the test method detection limits (i.e., MDL, RDL and LOQ) can be used to address the first two questions. Addressing the third question requires a knowledge of the test method precision function. Very few laboratories have determined test method precision functions, but once determined, the application in calculating the uncertainty, U, for an individual test result is as follows:

- identify the reported test result x
- use the precision function (i.e., $s = mx + s_0$) to calculate the standard deviation, s, and identify the corresponding degrees of freedom (e.g., n - 1)
- identify the desired confidence level (e.g., 95% or 99%) and the appropriate t statistic (two sided test)
- calculate the uncertainty, U, of the reported test result, x, by using $U = \pm ts$. The % relative uncertainty is given by $\pm 100\ ts/x$.

Note also that the above process can be used to produce a plot of % relative uncertainty versus analyte concentration, x, as shown in the following diagram.



The above diagram shows that high concentration data will have a limiting % relative uncertainty (given by 100tm). However, low concentration data are characterized by extremely large relative uncertainties that change significantly with incremental changes in the concentration. It is because of this extreme variation that interpretation of low level data is enhanced, when possible (by use of the precision function), to estimate the uncertainty of a reported test result.

Appendix 3: Summary of Laboratory Responses to Survey of Detection Limits

Parameter Group	Test Method	Responses (No. of Labs)
Metals	AA Flame	14
	ICP	46
	AA Graphite	12
	ICP - MS	8
	AA - Hydride	6
Mercury	AA - Cold Vapour	8
Cyanide	Colorimetric	40
Ammonia	Colorimetric	6